

Picosecond-jet Spectroscopy and Photochemistry

Energy Redistribution and its Impact on Coherence, Isomerization, Dissociation and Solvation

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The development of the picosecond-jet technique is presented. The applications of the technique to the studies of coherence (quantum beats), photodissociation, isomerization and partial solvation of molecules in supersonic-jet beams are detailed with emphasis on the role of intramolecular energy redistribution. Experimental evidence for intramolecular *threshold effect* for rates as a function of excess molecular energy is given and explained using simple theory for the redistribution of energy among certain modes. Comparison with R.R.K.M. calculation is also made to assess the nature of the statistical behaviour of the energy redistribution.

INTRODUCTORY REMARKS

The dynamics of vibrational energy flow in *large* and *isolated* molecules following selective laser excitation is very interesting and challenging for many reasons. From a theoretical point of view one would like to know how the coupling between bond vibrations influences the energy flow, and at what energy threshold does this flow or redistribution of energy from one mode to another occur. The energy region in which randomization or “chaotic behaviour” dominates is relevant to mode-selective chemistry.¹

Experimentally, a number of classical studies have been designed to examine the dynamics of vibrational energy in the S_1 state² of molecules in gas “bulbs” at low pressures, *i.e.* isolated in the sense that time between molecular collisions is longer than the experimental timescale. However, these large molecules at the bulb temperature have very large thermal energy, and coherent (or incoherent) excitation by a light source will suffer from the problem of sequence congestion. With the more recent (revisited) beam or jet techniques, one can vibrationally and rotationally cool these molecules and obtain the dispersed fluorescence or the excitation spectra. As shown from a number of important studies,^{3–6} excitation and fluorescence spectra at all times (more precisely using tens of nanoseconds resolution or using c.w. laser excitation) provide information on the high-resolution excited-state spectra, the geometry of van der Waals complexes and clusters, and in some cases the gross features of interstate coupling (line broadening etc.).

Our own interest has focused on the development^{7–13} of the picosecond-jet technique to study the time-resolved dynamics following the picosecond excitation of isolated molecules in supersonic jet beams. This technique was applied to a number

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of problems dealing with isomerization, dissociation, stepwise-solvation, hydrogen bonding and coherence. Here we shall highlight the new findings we obtained from these different studies, with particular emphasis on the relevance of these observations to vibrational energy redistribution (statistical R.R.K.M.-type as against non-statistical) and dephasing in isolated molecules.

THE PICOSECOND-LASER-MOLECULAR-BEAM APPARATUS

The arrangement we used for interfacing the picosecond laser to the molecular beam (or free jet) is shown schematically in fig. 1. The laser is a synchronously pumped dye-laser system whose coherence width, time and pulse duration were characterized¹⁴ by the SHG autocorrelation technique. The pulse widths of these lasers are typically 1–2 ps, or 15 ps when a cavity dumper is used. For detection one of three techniques

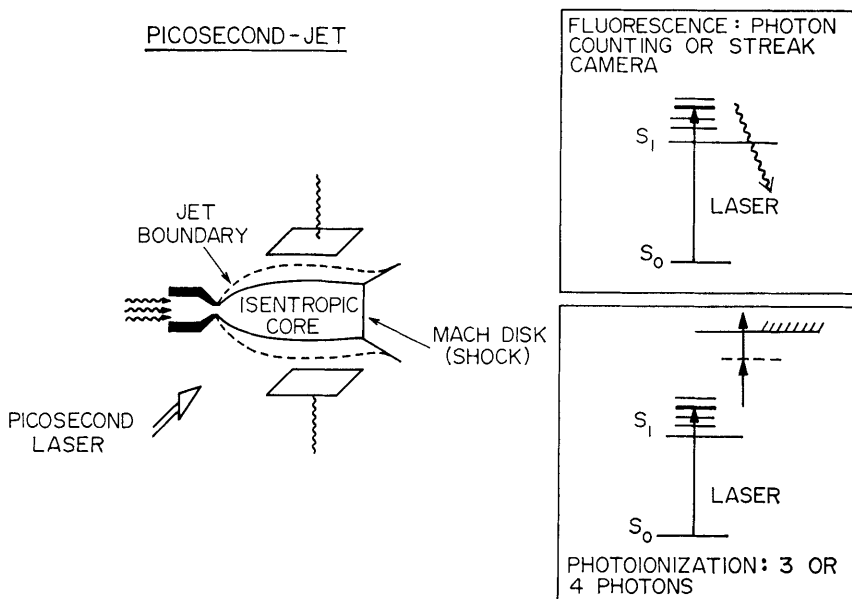


Fig. 1. An outline of the picosecond-jet technique and detection methods.

can be used: (a) Time-correlated single-photon counting (dispersed fluorescence) using a fast photomultiplier (or microchannel plate)—this way we achieved a resolution of ca. 100 ps (h.w.h.m.) *without* deconvolution. With deconvolution, one obtains, if required, the 30–50 ps time constants of single exponential decays. (b) Streak camera—a synchroscan streak camera gives a resolution of better than 10 ps with a repetition rate of up to 200 MHz. (c) Multiphoton ionization—we are using this technique (see fig. 1) to obtain the short-time behaviour, being limited by the pulse width of the laser (1 or 15 ps). This was applied to the stilbene isomerization problem.

Finally, the actual laser bandwidth was varied by using a combination of intra-cavity filters and etalons. In all these experiments the vibrational and rotational temperatures were typically <20–40 K and <10 K, respectively, depending on the molecular-beam conditions.

APPLICATIONS

(A) QUANTUM BEATS AND COHERENCE: ANTHRACENE, STILBENE AND PYRAZINE

The spectra of anthracene in a gas bulb at ca. 480 K reveal very little intensity of quasi-sharp lines (I_s) and a large background intensity that is very broad (I_b) or diffuse in nature. When anthracene is jet-cooled, I_s/I_b varies dramatically depending on the excess vibrational energy in S_1 . As shown in fig. 2, this ratio varies from 100 or

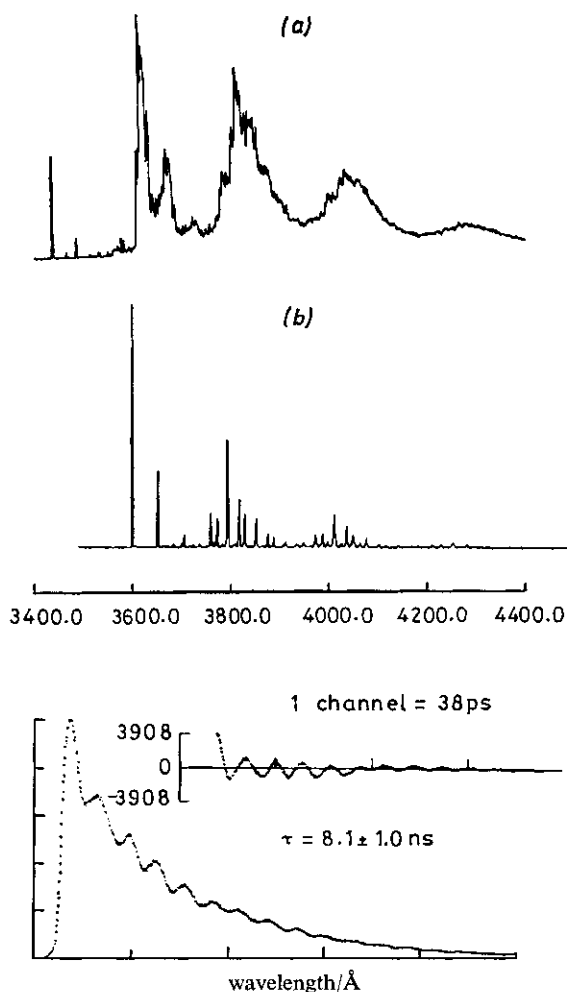


Fig. 2. Jet-cooled fluorescence spectra of anthracene at two excitation energies and quantum beats: (a) $E_x \approx 1400 \text{ cm}^{-1}$; (b) $E_x = 0$.

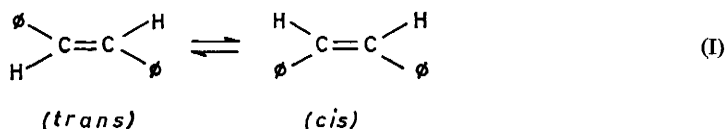
more at zero excess energy to 10^{-2} or less at 5600 cm^{-1} ; the spectra in the high-excess-energy (E_x) region are very similar to the bulb spectrum.

At $E_x \approx 1400 \text{ cm}^{-1}$ of excess energy in anthracene, we observed quantum beats in the dispersed fluorescence with a large modulation depth. The beats' modulation depth is sensitive to the excess energy and to the fluorescence detection wavelength.

(This work is now completed and will be published elsewhere.) For stilbene, the quantum beats appeared at a number of different E_x . Clearly, the observation of beats in these large molecules is related to the coherence of the vibrational-rotational states excited, a point that we shall discuss later. The beats, due to rovibronic states, in anthracene are not expected to be sensitive to magnetic fields. In a recent work we reported⁸ on the Zeeman effect on quantum beats in pyrazine, and on the importance of beats in unravelling the coupling of singlet and triplet rotational levels. In a more recent study by Kommandeur's group¹⁵ the high-resolution frequency spectra of pyrazine were observed and compared with our Fourier-transform beat spectra; excellent agreement was found. Finally, it should be emphasized that the origin of the beats in stilbene or anthracene is different from pyrazine; the former being directly related to the rotational-vibrational energy redistribution problem to be discussed later.

(B) ISOMERIZATION OF STILBENE

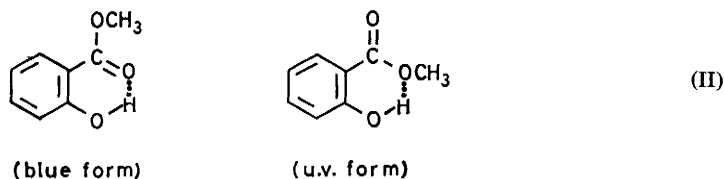
The isomerization process (I) involves some torsional vibrational modes for the twisting to finalize. This is a classical problem in chemistry, and much work has been done in solution¹⁶ and more recently under gas phase isolated molecule conditions.¹⁷ We have shown recently that the jet-cooled spectra¹⁰ of *trans*-stilbene displays the isolated molecule low-frequency modes which are optically active.



Furthermore, the observed¹⁰ rates measured as a function of excess energy (fig. 3) exhibit a *threshold* at ca. 1200 cm^{-1} , which is in very good agreement with the estimated barrier height for isomerization from S_1 in solution. The jet studies clearly indicate the absence of thermal energy influence on rates, and the involvement of the redistribution in the isomerization. We shall discuss this point later.

C. HYDROGEN-BONDED SYSTEMS

With the same technique we examined molecules which may be exhibiting proton transfer in the excited state. In other words in these molecules there exists the possibility of "tunnelling" between different configurations. The results for methyl



salicylate (blue form) in the jet show a drastic change in the equilibrium configuration upon excitation involving the OH, CO and low-frequency mode of 180 cm^{-1} . Furthermore, the observed fluorescence rate exhibits again a threshold at certain E_x ; from $(12 \text{ ns})^{-1}$ at zero E_x to $(160 \text{ ps})^{-1}$ at $E_x \approx 2000 \text{ cm}^{-1}$ (see fig. 4). We concluded from these studies that for the $E_x = 0$ excitation the distorted excited state is created simultaneously with the absorption of a photon in the *isolated* molecule. In the high

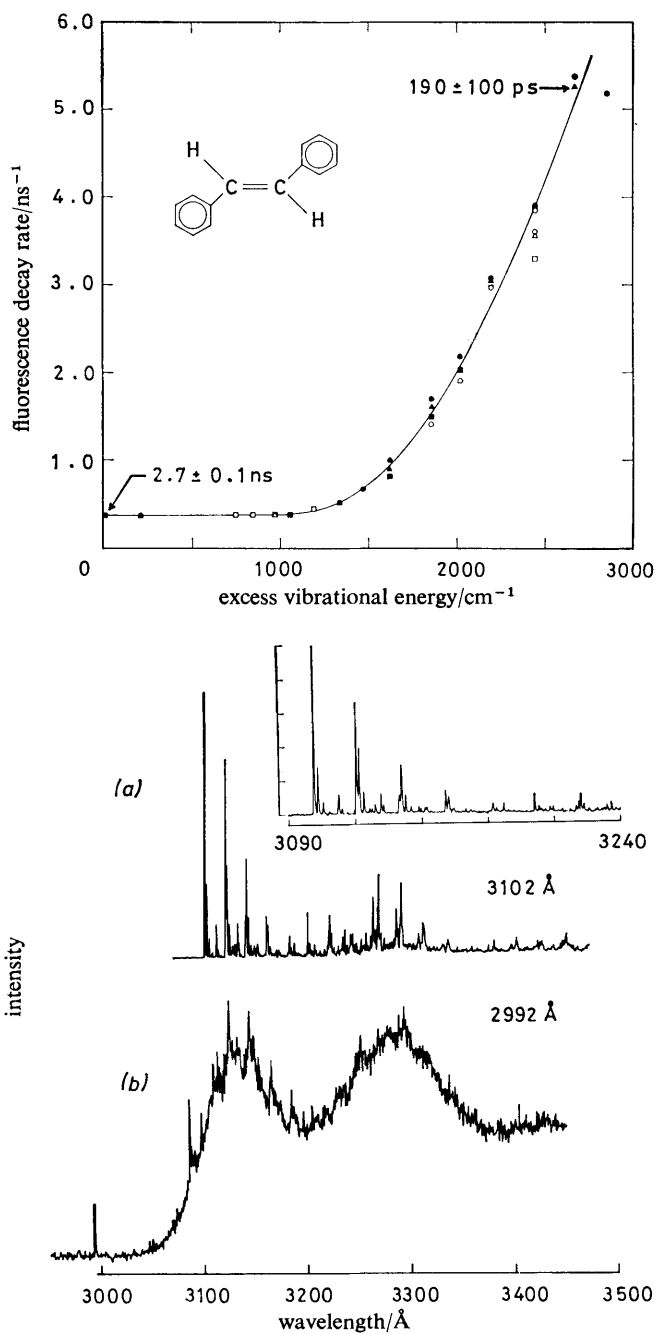


Fig. 3. Jet-cooled fluorescence spectra of stilbene [bottom (a) and (b)] and the threshold effect (top). Spectrum (a) is for 0,0 excitation.

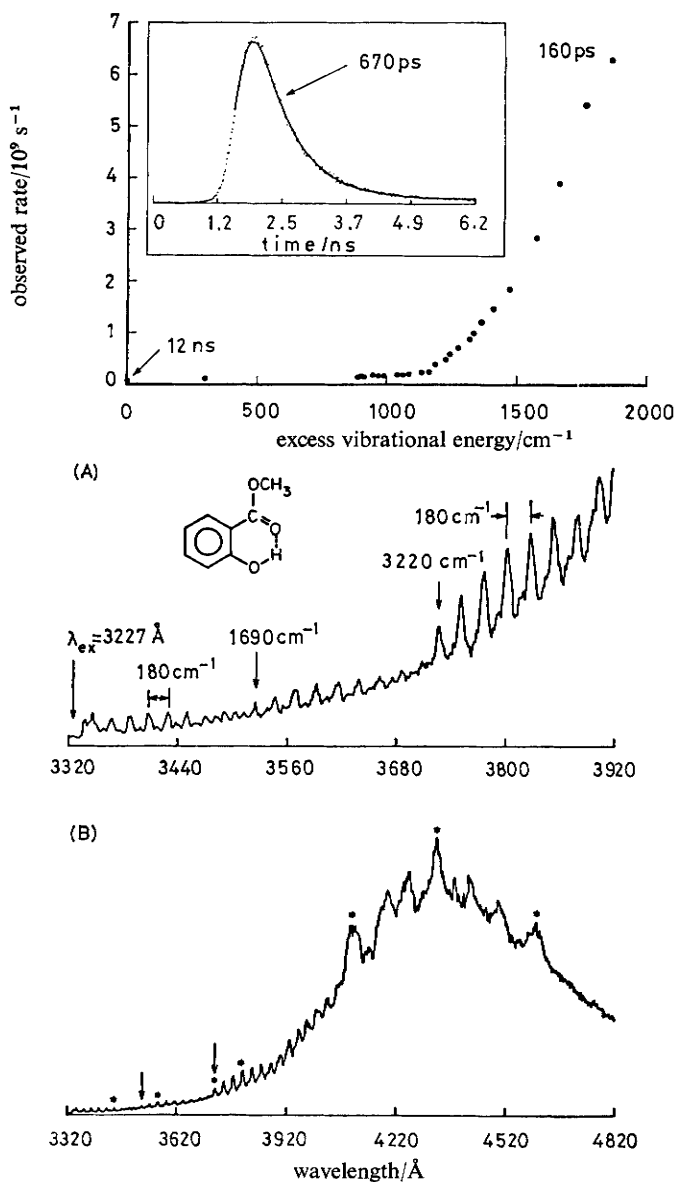


Fig. 4. Jet-cooled fluorescence spectra [bottom, (A) and (B)] and threshold effect (top) in MS.⁹

excess-energy limit, the low-frequency motions promote excited state electronic states coupling or configurational changes reminiscent of the stilbene problem. Thus the prevailing of the threshold effect as will be discussed later. We are currently studying the isotope effect on the dynamics.

(D) CHROMOPHORE-SELECTIVE PICOSECOND EXCITATION

The idea of this experiment is to excite a single chromophore in a molecule (jet-cooled) and to observe the real energy flow from the optically pumped vibrations of

this chromophore to other modes of the rest of the molecule. We chose the following molecule:



where A^* stands for excited anthracene and ϕ for an aniline group. This molecule was chosen because we already know a great deal about the redistribution problem in the "optically active" chromophore, anthracene, and also because this type of molecule has been extensively studied by the Columbia group and by others in solutions.¹⁸ In the jet we excite the different modes of the anthracene species with picosecond pulses and follow the time-resolved dispersed fluorescence of anthracene-like emission and product emission (red shifted emission due to the folding of the aniline species towards anthracene, charge-transfer or exciplex emission; henceforth referred to as "product"). At a given excess energy we observed a *decay* of the anthracene-like emission and a buildup in the product emission (fig. 5). These rates were found to be very sensitive to the excess vibrational energy in the anthracene chromophore! Thus, for the first time one can obtain the real-time measurement of product formation due to energy flow in an isolated large molecule.

Since the conformation change needed to give the red emission requires that the vibrational modes of the propyl linkage become populated, our results indicate that the excess vibrational energy in the anthracene species redistributes to vibrations (and "rotations") in the side chain, thus triggering the temporal behaviour of the molecule. The threshold for the excess-energy dependence of the product formation is ca. 1000 cm^{-1} (2.9 kcal mol^{-1}), consistent with a reaction barrier involving C—C type bonds (see fig. 5). Finally, as expected, the decay and buildup time constants at ca. 3000 cm^{-1} of excess energy (ca. 400 ps) are much different from the decay time constant of bare anthracene at similar excess energies (5.7 ns). The question then is: what does this rate in the isolated molecule mean and what is the role of the solvent?

Using an assumed set of vibrational frequencies for the molecule along with our jet lifetimes at different E_x , we have calculated the decay of the anthracene-like emission for a thermal distribution at 298 K. The calculated lifetime (ca. 600 ps) is appreciably shorter than actually observed in cyclohexane solution (1.4 ns).¹⁸ Thus it appears that the geometrical changes needed for product formation are hindered by the solvent.

Marcus and Noyes¹⁹ have discussed the effect of diffusion on observed reaction rates. Near steady state, $\tau_{\text{obs}} \approx \tau_{\text{activ}} + \tau_{\text{diff}}$. Consequently, the real τ_{act} can be shorter than that observed in solution. Since the diffusion coefficient is on the order of a few times $10^{-5}\text{ cm}^2\text{ s}^{-1}$, it is perhaps not surprising for a diffusion distance of order of 10 \AA that $\tau_{\text{diff}} \approx 1\text{ ns}$, and τ (isolated molecule) $\approx 500\text{ ps}$. More tests of these ideas are in progress. The important point, however, is that energy redistribution to the propyl linkage occurs and product formation has a threshold at ca. 1000 cm^{-1} . As shown in fig. 5 the rate of product buildup is the same as that of the anthracene chromophore decay.

(E) STEPWISE SOLVATION AND PHOTODISSOCIATION

Last year we extended the application of the picosecond-jet technique to the study of the dynamics of isolated molecules in various stages of solvation with various solvents (water, alcohol, etc).^{13,20} The idea was to study this "controlled" solvation and its dependence on the energy redistribution. Also we wanted to examine the photodissociation of these different solvated species or complexes following selective pumping by the picosecond laser. The systems we studied in some detail are azine-solvent complexes made in the jet with He or Ar as the carrier gas.

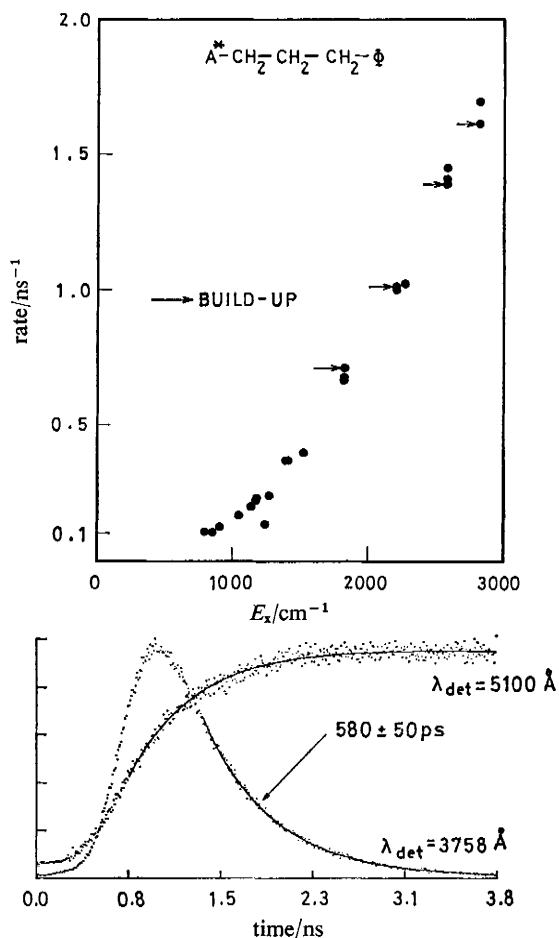


Fig. 5. For caption see opposite.

From the dispersed fluorescence, excitation spectra and their dependence on solvent concentration we identified the different solvated species and obtained the frequency of the new vibrational modes that result from complexation (typically 170 cm^{-1} and below). For isoquinoline (IQ) three solvents were used (water, methanol and acetone) to deduce some particular effects regarding the nature of hydrogen bonding in the species:

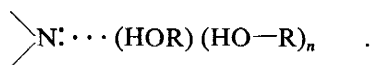


Fig. 6 and 7 display typical results for the effect of solvent on the excitation spectra, fluorescence and lifetimes. We used these observations to measure bond dissociation energy of the different species by varying the excess vibrational energy of the "parent" jet-cooled molecule type modes. The threshold effect found for the dissociation of the 1:1 IQ (methanol) is evident and occurs at ca. 3 kcal mol^{-1} , in agreement with solution-phase enthalpies. (The effect of higher degree of solvation on the dynamics will be discussed elsewhere.)

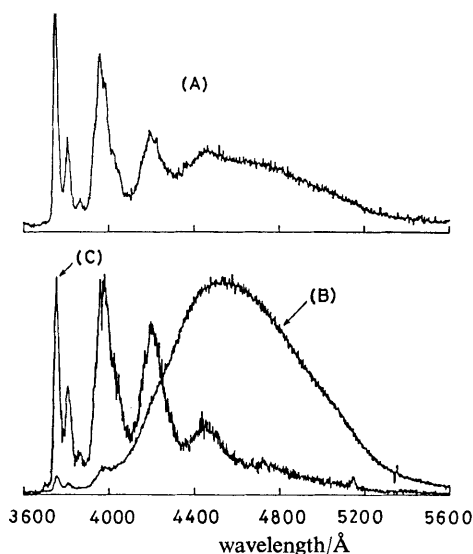


Fig. 5. Threshold effect (facing page, top) and fluorescence spectra at different E_x . Facing page, bottom: decay of anthracene-like emission and build-up of product emission. This page: fluorescence spectra at early and long gating times after the pulse. Note the evolution of the product emission with time.¹¹ (A) All times, $E_{\text{exs}} \approx 1400 \text{ cm}^{-1}$; (B) all times, $E_{\text{exs}} \approx 2800 \text{ cm}^{-1}$; (C) early time $E_{\text{exs}} \approx 2800 \text{ cm}^{-1}$.

SOME THEORETICAL IDEAS

(A) HOMOGENEOUS BROADENINGS IN ISOLATED MOLECULES

As is well known, one cannot observe quantum beats unless the separation between energy states is larger than or comparable to the width of these states (or bunch of states). In anthracene the results of Lambert et al.⁷ (see previous section) must therefore indicate that the rovibronic states prepared by the laser pulse (at the measured excess vibrational energy) are not severely overlapping. In fact, a limit on the homogeneous width is now available: $< 500 \text{ MHz}$. The apparent width of the excitation spectra is, of course, much larger (implying picosecond relaxation) than this width, but, in principle, by using single-mode laser excitation we should be able to resolve bands that correlate with the beat frequency, especially in the resonance fluorescence region. In this region there is no complexity due to the presence of many levels in the final state of the emission.

The interesting findings in anthracene are: (a) the uniqueness of the observation of beats at certain excess energy and the sensitivity of the observation to detection wavelengths; (b) the shortening of lifetimes at higher E_x . These lifetimes do not vary drastically in magnitude even though the dispersed fluorescence broadens in a dramatic way at higher E_x values. Actually, the "broad" feature of the dispersed fluorescence is *not* a real continuum. This suggests that the final state of the emission could be highly structured. To clarify the involvement of the final state (or states) in the observed spectra (hence the nature of vibrational redistribution) Keelan²¹ is examining the effect of density-of-states in the initial and final manifolds, and couplings on the overall redistribution.

The reason that these beats are sensitive to excitation and detection energies is clear. For the excitation process we must form linear combinations of these rovibronic

states in order to see the interference (coherent) effects. The laser source, which was varied with respect to coherence time and width, has pulse substructure with each of the "noise" spikes of the substructure having large enough bandwidth to span the excited states to form the superposition. If the damping is faster than the period of the beats, as it will be at high excess energies, then no beats will be observed. In the

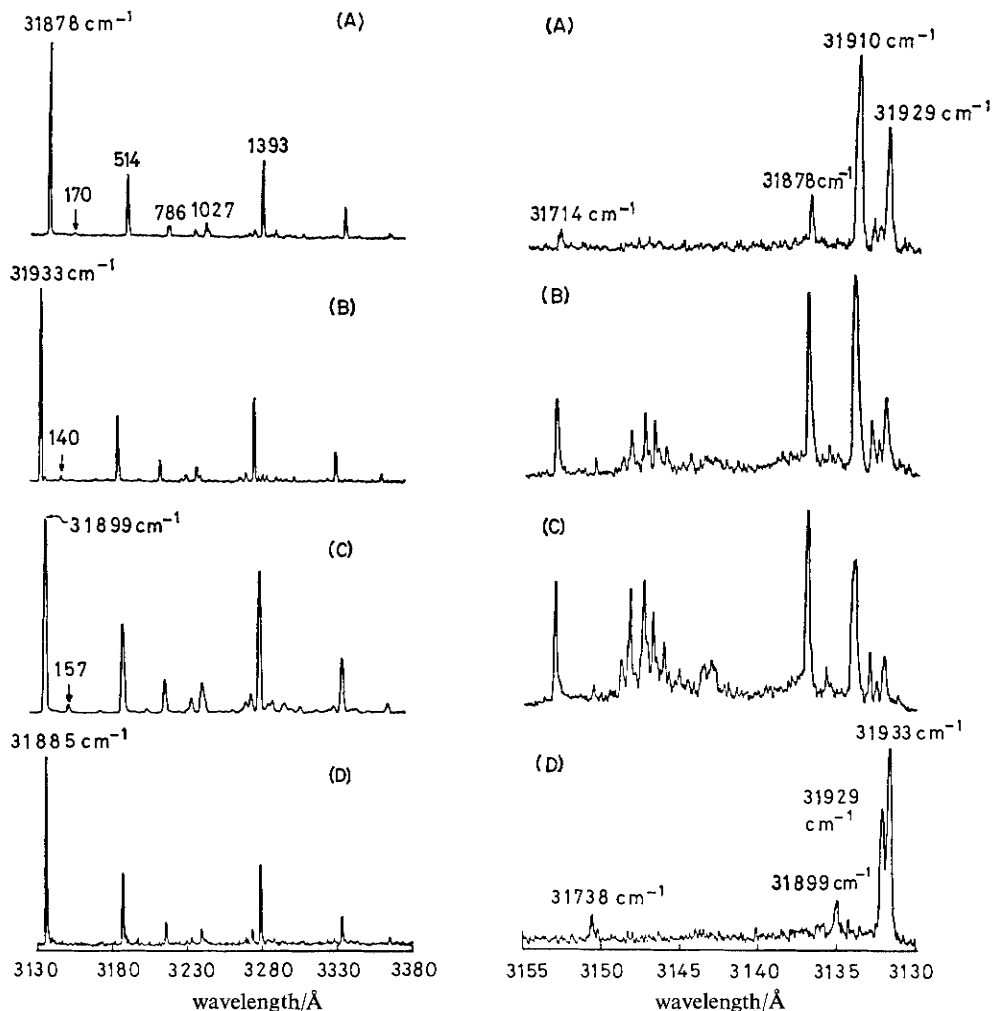


Fig. 6. Jet-cooled fluorescence spectra of IQ-solvent (left) and the excitation spectra (right) at different solvent concentrations. (A)–(C) on the right give excitation spectra at 4, 10 and 25 Torr methanol, respectively. (D) is the spectrum at 10 Torr water. On the left, (A) is for methanol-2, (B) and (C) for water-1 and water-2, and (D) for acetone. Details are given in ref. (13) and (20).

decay process, on the other hand, one must have branching transitions, i.e. a common level to the emitting states. If the oscillator strength of one of the beating levels to the final state is very different, the modulation depth will be altered. The modulation depth varies in our experiment, and one plausible explanation of the *nature* of the beating states is that there is a mode-specific Coriolis coupling at this excess energy.

This coupling will alter the relative oscillator strength of the emitting states, and will be specific depending on the K rotational structure. This should be evident in the very high-resolution Doppler-free spectra of anthracene, reminiscent of the benzene work of Schlag's group.²² It is also possible that rotationally averaged anharmonic coupling is present. The points will be addressed in a forthcoming paper (by

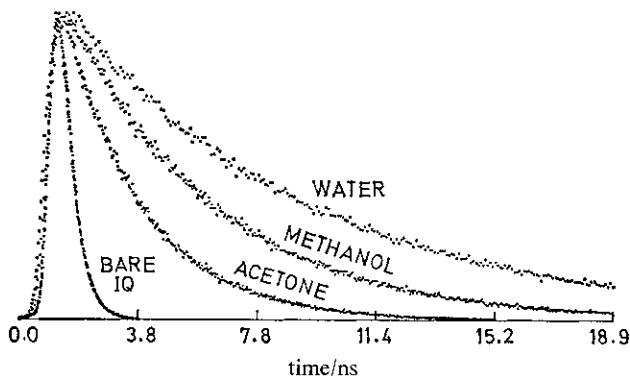


Fig. 7. Lifetimes of IQ-solvent complexes in the jet: water, 7.9 ns; methanol, 4.6 ns; acetone, 2.5 ns; bare IQ, 380 ps.

Lambert, Felker and Zewail) from this laboratory. The important point here is that whatever the nature of the states involved, it is clear that some strongly coupled vibrational states in the molecule at certain excess vibrational energies are coherent on subnanosecond time-scales, as evident from the data on anthracene and stilbene. Recently similar findings have been found for molecules in their ground electronic state but also with excess vibrational energy.²³

(B) THE "THRESHOLD" EFFECT AND REDISTRIBUTION BY LOW-FREQUENCY MODES

In our studies of anthracene, stilbene, methyl salicylate, $A-(CH_2)_3-\phi$ and photo-dissociation in the jet, the following general features were found: (a) A threshold for an order-of-magnitude change in the rate at E_x between 1000 and 2000 cm^{-1} , depending on the molecule. In anthracene there is a levelling off of this rate at $E_x \approx 1500$ cm^{-1} and the change in the rate is only a factor of 4. (We have also studied the effect of deuterium substitution.) (b) Quantum beats in anthracene and stilbene are absent above the energy region for this abrupt change in the rate. (c) The dispersed fluorescence of anthracene around this threshold area displays two features—a sharp resonance emission and a "diffuse" red-shifted [from a (0,0) excitation] emission. The spectra become completely diffuse at high excess energies and resemble the trend found in other large molecules.

An interesting question arises from these studies: What is the origin of this threshold effect? In what follows some ideas are presented.

The initial temperature of the molecule is very low and certainly is much lower than $\hbar\omega/k$ of totally symmetric modes. We may divide the modes of the molecule into those which are optically active (predominantly totally symmetric or "relevant" R) and those which are not excited directly by the laser (bath modes B). This division of the system-bath interactions accounts for dephasing and energy relaxation by T_2 and T_1 time constants as discussed elsewhere.^{1,24}

The laser excites the totally symmetric R modes of anthracene but the molecule has a number of low-frequency (including non-totally symmetric) B modes (about ten) which range in frequency from 100 to 500 cm^{-1} . The redistribution of excitation of R

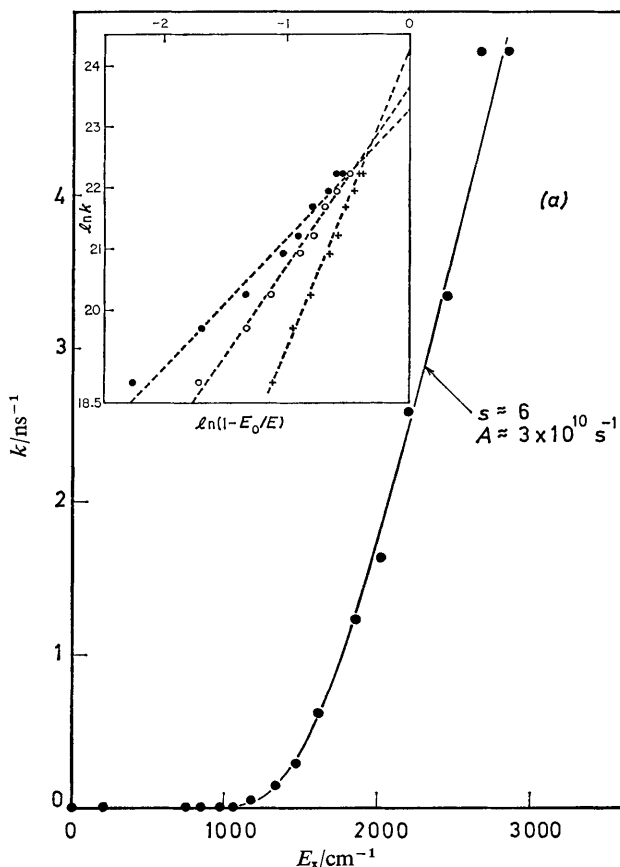


Fig. 8. For caption see opposite.

to B will have a threshold depending on the number of quanta that can be populated in B (density of states) and the degree of coupling. Invoking these low-frequency modes in the redistribution suggests the use of restricted density of states since high frequency modes are not efficiently populated. It is interesting that in all molecules we studied such modes do exist, and it is perhaps a universal character of these large molecules to involve these modes in the redistribution. The change in anthracene rates around the threshold is not as dramatic as in the other molecules which enjoy more of these low-frequency modes. The "suppression" of the activity of these modes by the Shpolskii effect in matrices may be the reason for obtaining sharp spectra, or in our language, in enhancing the I_s/I_b ratio. The question is now: Knowing the mode structure, can we predict theoretically the energy threshold effect?

(C) STATISTICAL AND SIMPLE THEORIES FOR THE REDISTRIBUTION

Here we shall outline an approach that is simple, but perhaps too simple. For the redistribution, we will define a redistribution parameter ("temperature") which describes the rate according to the following equation:

$$k = Ae^{-E_0/kT_{\text{eff}}} = Ae^{-\bar{n}E_0/E_x}$$

where \bar{n} is the average number of modes (restricted number of modes) that the molecule "heats up" in the redistribution. If this is a real heating process, the analogy with

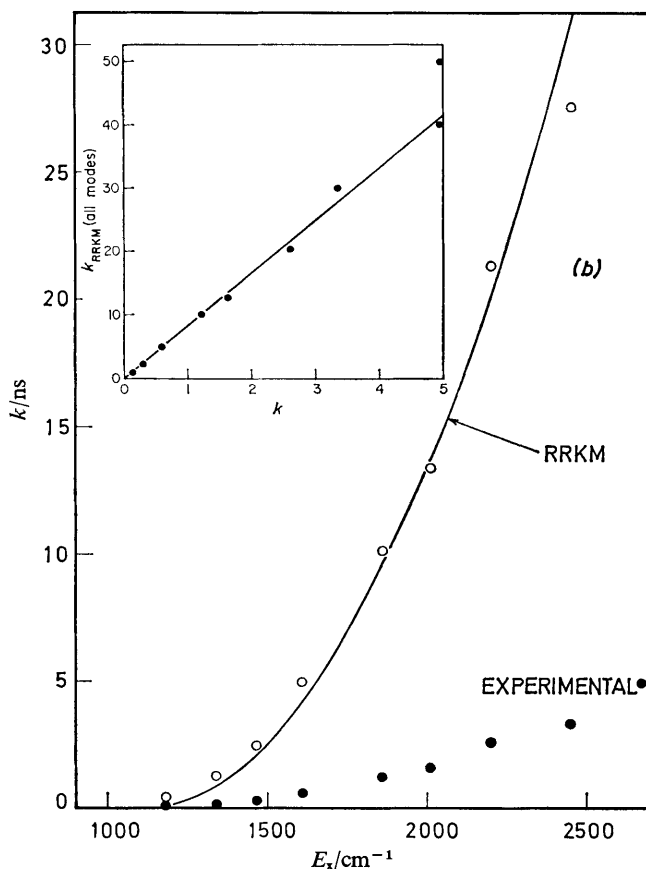


Fig. 8. (a) The fit of the stilbene data to R.R.K. theory. The insert shows the sensitivity of the fit to the E_0 value. $+$, $E_0 = 900 \text{ cm}^{-1}$; \circ , $E_0 = 1100 \text{ cm}^{-1}$; \bullet , $E_0 = 1200 \text{ cm}^{-1}$. (b) Comparison of the R.R.K.M. calculation for stilbene with our data. When the experimental data are scaled by α , the agreement with R.R.K.M. theory is quite good. We ascribe α as due to reversible isomerization process at the E_x of interest. \bullet , Observed rates; \circ , scaled rates (αK_{obs} ; $\alpha = 8.3$). The plot of $\ln k$ against $1/E_x$, not shown, gives a straight line.

solids for the use of specific-heat will give an effective number of modes. When we plotted experimental $\ln k$ against $1/E_x$ for stilbene (see data of fig. 3) we obtained a very good straight-line fit with a "pre-exponential" of ca. $1.5 \times 10^{11} \text{ s}^{-1}$, and an apparent activation energy of ca. 9000 cm^{-1} . Since E_0 is known from our work to be ca. 1000 cm^{-1} , which is in good agreement with solution-phase studies of the isomerization rate, $n \approx 9$. This number is in surprisingly good agreement with the above "naive" prediction and with the number of low-frequency modes ($< 500 \text{ cm}^{-1}$) which are known for stilbene. It should be mentioned that when we used the classical R.R.K. expression * for k , we obtained from the fit of the data $S \approx 6$ and $E_0 \approx 1000 \text{ cm}^{-1}$.

* The R. R. K. expression is simply

$$k = \nu \left(\frac{E - E_0}{E} \right)^{S-1}$$

where S is the number of vibrational oscillators.

(fig. 8). (One can show that the R.R.K. expression can be written in an exponential form.) Applications of this idea to other systems are underway.

In a collaborative effort with Marcus, we used quantum calculations of the density of states to obtain the rates that are in accord with the R.R.K.M. theory. We have found the following: First it can be shown that the E_0 obtained from our experiments (k against E_x) can be correlated with that obtained from solution-phase studies ($k \approx Ae^{-E_0/kT}$). Secondly, deviations from R.R.K.M. can be handled by

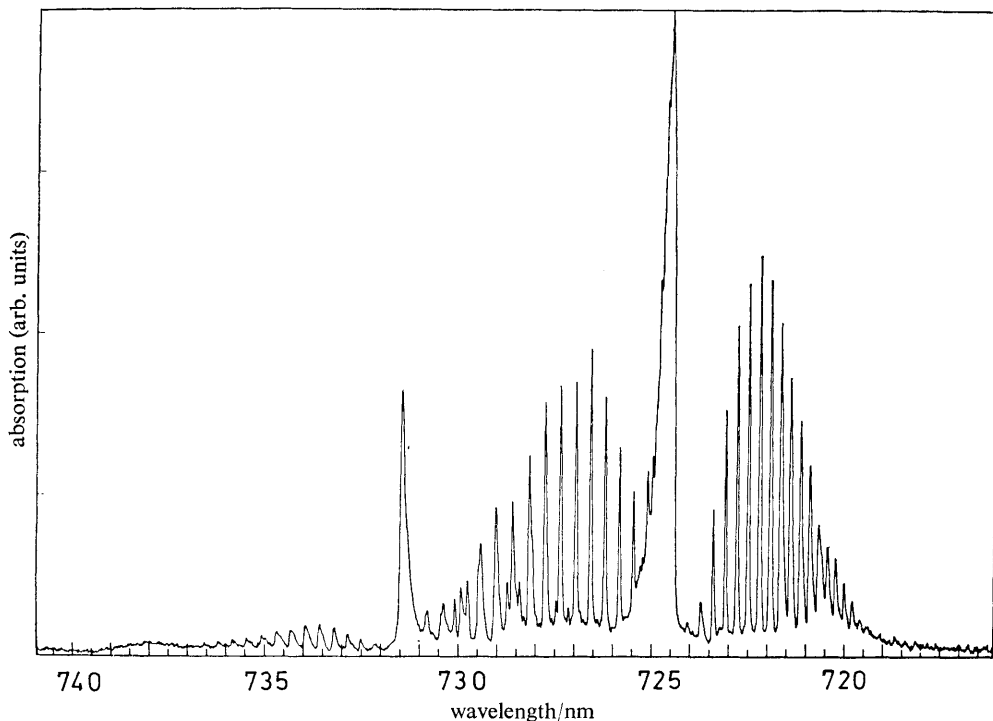


Fig. 9. The overtone spectrum of CHD_3 in the gas phase at $\Delta\nu_{\text{CH}} = 5$. Note the well resolved P, Q, R branches. The presence of two Q branches is due to Fermi resonance interaction.

using the appropriate modification in rates in order to suit these new observations. These modifications include reversible rate processes for the isomerization at these excess energies and trapping of energy in certain coordinates in the transition-state configuration.

For the dissociation of IQ-water and IQ-methanol good agreement with R.R.K.M. theory was found. In these systems there are numerous low-frequency modes due to complexation, and the density of B-type modes (states) is very large. This work will be published elsewhere.

In conclusion, the measurements of rates as a function of E_x in the beam provide a way of obtaining the threshold energy ("solvent free") and the redistribution among modes. It is possible that B-type modes are the main constituents of the phase space for the redistribution, and that this effect is almost universal. It is interesting that the effective-temperature idea for k as a function of E_x will predict that at ca. 2000 cm^{-1} of excess energy the effective temperature is approaching room temperature, consistent with redistribution and congestion of spectra. These studies raise interesting

new questions regarding these possibilities and more experiments are in progress to test these ideas. Finally, the studies of stepwise solvation in beams promise interesting new avenues in that we may learn about linkages between gas-phase and solution chemistry from a microscopic point of view.

(D) WHAT ABOUT THE HIGH-ENERGY REGION?

Until now we have not obtained real-time measurements in the high-energy region (2 eV or so). However, in a recent experiment by Perry et al.²⁵ we have examined the spectra (fig. 9) of the molecule CHD₃ where there is only *one* CH local-mode oscillator that can couple to all other modes. Several interesting points emerge from the studies. First, the spectra $\Delta\nu_{\text{CH}} = 6,7 \dots$ etc. are incredibly sharp even in the very high-energy region (ca. 16 000 cm⁻¹). Secondly, the rotational pattern basically prevails except for Fermi resonance type interactions. Thirdly, the transition line-width of the isolated molecule (low-pressure) gives a relaxation time *longer* than ca. 1 ps. Using the same theoretical ideas discussed above for the threshold effect ρ_t at this excess ground-state vibrational energy (16 000 cm⁻¹) is only ca. 40 cm, which is the range at which we expect the redistribution rate to be different in magnitude from that at lower energies (the number of states at 5000 cm⁻¹ is few). This means that the threshold should be at much higher energies than those described for the other large molecules in S₁. (In contrast, benzene at 16 000 cm⁻¹ shows $\rho_t \approx 2 \times 10^8$ cm.) Consistent with this idea is the fact that the rotational constant as a function of excess energy undergoes a marked change about this threshold energy. More discussion of the energy distribution problem at high energies is given in ref. (26).

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